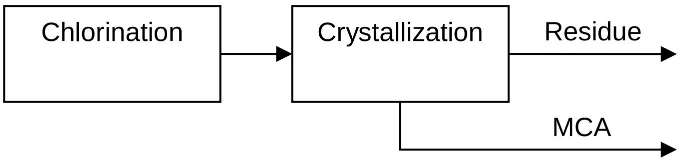
Purification of Monochloroacetic Acid by Hydrogenation

1. Dichloroacetic acid as side product

Most manufacturers use the chlorination route to react acetic acid (Ac) with chlorine to produce monoacetic acid (MCA) using acetic anhydride (AA) as catalyst. During the reaction, monoacetic acid is further chlorinated to dichloroacetic acid (DCA).

The crude MCA stream after chlorination contains about 2-3% DCA. Many applications require low content of DCA (less then 0.1%). So the crude MCA solution has to be purified.

Almost pure MCA can be obtained by fractional crystallization. MCA has a melting point of 61 °C while DCA and Ac have melting point of 9-11 and 15 °C. In the crystallization step, MCA is produced with over 99% purity:



The residue contains typically about MCA 70%, DCA 20%, Ac 7% and water 3%. In some process, the residue is further treated to recover acetic acid and generated a stream containing mainly MCA 65% and DCA 35%.

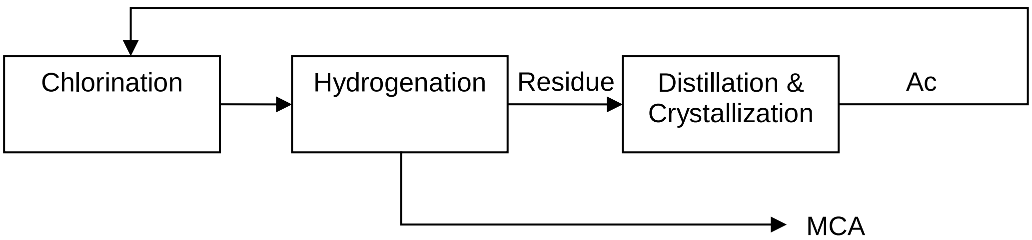
MCA and DCA have very closed boiling point and is almost impossible to separate by distillation. This problem can be solved by catalytic hydrogenation of DCA to MCA:

2. Hydrogenation of DCA to MCA

Buss ChemTech AG developed processes to hydrogenate DCA to MCA. There are two different routes:

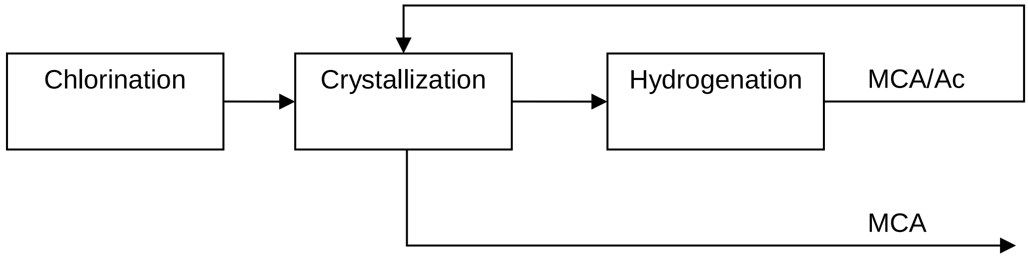
Route 1

The crude mixture MCA/DCA is directly hydrogenated to transform DCA mainly to MCA, followed by crystallisation and distillation of residual acetic acid.



Route 2:

The route 2 starts with the fractional crystallisation. Only the the residue from the crystallization is hydrogenated to remove DCA and return the resulting product back to the crystallization section.



Comparison of the two Routes:

Route	**hydrogenation reactor**	**distillation column**	**investment**	**total yield MCA**
1	large	to remove Ac	higher	higher
2	3 times smaller	not needed	lower	lower

3. Performance

Both routes can produce high purity MCA while the product from route 1 will contain less acetic acid. The catalyst can be deactivated by iron containing in the feed stream, so the iron has to be removed before hydrogenation.

Route 1

Specifications	
Crude MCA	
MCA	> 94%wt
DCA	3 ~ 4%wt
Ac	< 2%wt
Water	< 0.5%wt
Fe+	< 10 ppm
MCA after hydrogenation	
MCA	> 96 ~ 97 %wt
DCA	< 0.05 %wt
Ac	3 ~ 4 %wt
MCA product	
MCA	> 99.7 %wt
DCA	< 0.05 %wt
Ac	0.1 ~ 0.2 %wt
By product	HCl 30%

Consumption Figures*	
Hydrogen	29 Nm^3
Nitrogen	20 Nm^3
Cooling water	75 m^3
Steam	400 kg
Chilled water (-20ºC)	3.5 m^3
Electricity	65 kWh
Process water	74 kg
Catalyst	100 g
*per t of product, incl. hydrogenation and distillation	

Route 2

Specifications	
Residue Stream	
MCA	60 ~ 70 %wt
DCA	30 ~ 40 %wt
Ac	< 2%wt
Water	< 0.5%wt
Fe+	< 10 ppm
MCA after hydrogenation	
MCA	> 95 ~ 97 %wt
DCA	< 0.05 %wt
Ac	3 ~ 5 %wt
By product	HCl 30%
The quality of Final MCA product is determined by the crystallization section.	

Consumption Figures*	
Hydrogen	97 Nm^3
Nitrogen	23 Nm^3
Cooling water	175 m^3
Steam	460 kg
Chilled water (-20ºC)	5 m^3
Electricity	135 kWh
Process water	310 kg
Catalyst	150 g
*per t of product, based on 65:35 MCA:DCA residue stream	